IMPROVING SNR IN TIME-RESOLVED SPECTROSCOPIES WITHOUT SACRIFICING TEMPORAL-RESOLUTION: APPLICATION TO THE UV PHOTOLYSIS OF METHYL CYANOFORMATE

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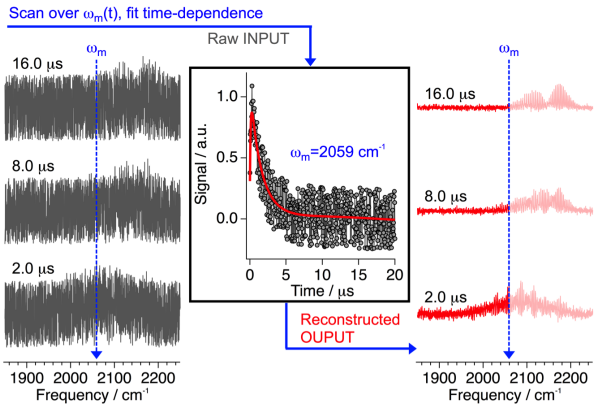
We demonstrate a new analysis for the enhancement of the signal-to-noise ratio (SNR) in time-resolved spectroscopies, termed spectral reconstruction analysis (SRA). As distinct from a simple linear average which produces only a *single* representative spectrum with enhanced SNR, SRA produces a comparable enhancement, but fully preserves the measured time-dependence. Specifically, given a series of (n) time-resolved spectra, SRA yields an approximate *sqrt(n)* SNR enhancement for each of the original n-spectra. SRA operates by eliminating noise in the temporal domain, thereby significantly attenuating noise in the spectral domain, as follows (see Figure): Temporal profiles of each measured frequency are fit to capture the representative temporal evolutions, then time-resolved spectra are reconstructed by replacing the measured profiles with the fit profiles.



In addition to simulated control data sets, we demonstrate SRA with experimentally measured time-resolved IR emission spectra, collected following the 193 nm photolysis of methyl cyanoformate ($CH_3OC(O)CN$). Of significance, we now show the appearance of resonances assignable to hydrogen cyanide (HCN), which were previously obscured in the noise of the measured spectra. The presence of HCN suggests the occurrence of a previously uncharacterized dissociation channel, likely involving a cyclic 5-center transition state.